BUCKYCARBONS AND FULLERENES IN INTERPLANETARY DUST PARTICLES BASED ON EVIDENCE FROM A TRANSMISSION ELECTRON MICROSCOPE (TEM) STUDY OF VAPOR CONDENSED CARBONS WITH VARIABLE C/H RATIO. Frans J.M. Rietmeijer[1], Alessandra Rotundi[2,3], L. Colangeli[3], V. Mennella[3], P. Palumbo[2] and E. Bussoletti[2], [1]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, USA; [2]Istituto di Fisica Sperimentale, Istituto Universitario Navale, Via A. de Gasperi 5, I-80133, Naples, Italy; [3]Osservatorio Astronomico di Capodimonte, Via Moiariello 16, I-80131, Naples, Italy.

Extraterrestrial buckminsterfullerene (C_{60}) was identified in the Allende meteorite [1] and an impact crater on the LDEF satelllite [2]. The X-XANES analyses of interplanetary dust particle (IDP) L2008F4 have not yet found C_{60} [3]. Amorphous and poorly graphitised carbons, PAHs, and rare graphite and hexagonal diamond in IDPs were determined by a range of experimental techniques [4], including TEM. Following the discovery of C_{60}, fullerene-related carbons such as 'buckyonions', 'bucky(nano)tubes', and polyhedral structures of concentric (002) layers were indentified [5] and the concentric circular, poorly graphitised carbons in the Allende meteorite [6] were reinterpreted as 'buckycarbons'. Similarly, 'buckyonions', 'buckytubes', and loop-in-loop rings that are cross-sections of compound 'buckyonions' [*cf.* ref. 7], also occur in some chondritic IDPs [8,9]. We note that polycrystalline, or 'ring', selected area electron diffraction patterns for carbon blacks and samples of 'buckycarbons', when using a field limiting aperture larger than the modal size in the sample, show the same broad (*hkl*) 00*2*, 10*l*, and 11*l* rings. Electron diffraction alone cannot distinguish these morphologically unique pre-graphitic carbons. An identification as poorly graphitised carbons implies that they are the products of prograde thermal metamorphism of hydrocarbons while the information carried by 'buckycarbons' is fundamentally different, *i.e.* they may be vapor phase condensates.

OBSERVATIONS. Our TEM study of C/H carbon smokes produced in atmospheres ranging from pure Ar to Ar/H_2=7/3 has found several carbon structures, *viz.* (*i*) carbon smoke, (*ii*) tangled networks of fine-grained [1-3 (002) layers] and coarse-grained (~2 - 5.5 nm) (002) ribbons, (*iii*) a profusion of 'buckyonions' and hollow 'buckytubes' ranging from needles to stubby units closed at both ends by curved, polygonal and cone shaped caps [10], (*iv*) coarse-grained polyhedral 'buckyonions' with up to 30-40 concentric (002) layers and 'buckytubes' with complex internal ('traversing' [5]) layer growth morphology [ref. 7], (*v*) open and compact, polyhedral scroll-type structures (~50-100 nm in diameter) of (002) ribbons with increasing thickness (~1-10 nm) from the center outwards, (*vi*) featureless polyhedral plates < 90 nm, and (*vi*) hexagonal, single-crystal carbon plates (< 500 nm) with an *a*-axis of 0.52 nm.

The polyhedral plates, the compact scroll-type structures and the hexagonal single-crystal plates occur in very low-hydrogen carbons that were produced by (*i*) condensation in a H_2-free atmosphere, and (*ii*) thermal annealing at 800°C of H-bearing carbons to drive off hydrogen [11]. The polygonal plates recrystallised at 700-800°C to hexagonal plates. The presence of other carbon structures is not obviously affected by the C/H ratio. The carbon interrelationships in the samples support that condensation of the coarse-grained polyhedral 'buckycarbons' and scrolls was followed by amorphous carbons that developed into the tangled networks. Rare 'buckyonions' have an amorphous carbon rim. We also analysed C_{60} and C_{70} samples (provided by D. Heymann) that consist of hexagonal single-crystal plates. The measured C_{60} unit cell data match the reported values [12] for this molecular carbon.

DISCUSSION. A summary of literature data suggests to us that thermal annealing of carbonized carbons may take different tracks depending on whether the starting materials are hydrocarbons or pure carbons. The former was well studied by XRD and TEM studies [*cf.* 13]. The latter received considerable interest as part of the ongoing research on fullerene-related carbons. During the initial stages of heat treatment both types of starting materials develop similar tangled networks of graphitic ribbons of only a few basal layers thick that coarsen with continued heat treatment [13,14]. With further thermal annealing, a carbon soot developed (sub)circular closed loops of 2-8 carbon shells, at 1700°/1 h 'buckyonions' with polyhedral cross-sections at 2400°/4 min, and nanotubes closed at both ends [14]. Nanotubes are polygonized as a function of tubule thickness [15]. Polygonization of the fullerene-related carbons is due to (1) defects in the growth of aromatic layers by insertion of a pentagon or heptagon [15,16] and introduction of sp^3 bonds, either locally to relieve strain of the trigonal sp^2 state [7] or linear arrays [5] that causes bending at 60° and 120° angles in polygonal 'buckycarbons'.

A vapor condensed smoke consists of kinetically-controlled, high-temperature solids, *e.g.* tridymite in Si_xO_y [17] that formed during condensation proper and autoannealing of quenched liquid condensates. Iijima [7] suggested that the hollow center of concentric circular structures (*i.e.* 'buckyonions') is due to the liquid to solid carbon volume change but it is not clear how this interpretation explains the varied morphologies of 'buckytubes'. To evaluate the presence 'buckycarbons' in vapor-condensed carbons, it is germane to consider the thermal annealing of carbon soot [14] suggesting that 'buckycarbons' may be a high-temperature carbon allotrope with an effective volume much closer to the liquid than to that of the solid. If our interpretation is correct 'buckycarbons' will be a favored phase in pure carbon smokes.

The experimentally produced carbon structures (*ii*), (*iii*) and (*iv*) co-occur in chondritic IDPs [8,9] and support they condensed from pure to low-H_2 carbon vapors. The scroll-type carbons are pure carbons wherein growth defects in the aromatic layers introduced during rapid (molecular?) growth caused polygonization. Autoannealing of compact scrolls yielded polygonal sheets or platey hexagonal single-crystals in the thermally annealed sample. A simple interpretation of their unit cell parameters assumes a linear correlation between *a*-axis of graphite, C_{60} and C_{70}, or C_n where *n* is the number of atoms. This two-point correlation supports *n* = 23 % 3 in the hexagonal plates. We note that C_{20} was proposed as a precursor to C_{60} formation whereby the C_{20}

structure, *viz.* a closed cage, a cap, or a ring, is a function of the formation temperature [18]. The cap structure of five hexagons surrounding one pentagon is considered the seed upon which other fragments attach to form a complete closed C_{60} shell [18]. C_{20} may have formed in our experiments at temperatures conducive to the cap structure at about 725°C, but the duration and/or temperatures of the experiments precluded C_{60} formation. It remains possible that curved PAHs, the intermediates in the conversion of planar PAH-type structures to curved fullerene-related structures, are necessary for C_{60} formation [19].

CONCLUSIONS. In our AEM study of vapor condensed carbons with variable C/H ratio we found abundant 'buckyonions', 'buckytubes' and loop-in-loop carbon structures that are similar to those in several chondritic IDPs. The introduction of defects during continuous rapid growth in the experiments produced the scrolls of carbon ribbons that were precursors to hexagonal C_{20} plates but that could not grow to form C_{60}. When our experiments indeed simulate carbon condensation under astrophysical conditions, our data support that in chondritic IDPs C_{60} will be rare but C_{20} could be a common pure carbon phase. Buckyonions and 'buckytubes' may abound and their presence does not constrain C/H ratios in the range we investigated. Post-accretion thermal annealing, *i.e.* dynamic pyrometamorphism, may be required to produce C_{60} in pure elemental carbons in chondritic IDPs.

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